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MASS TRANSFER WITH COMPLEX REVERSIBLE CHEMICAL REACTIONS—II. PARALLEL REVERSIBLE CHEMICAL REACTIONS

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Abstract—An absorption model has been developed which can be used to calculate rapidly absorption rates for the phenomenon mass transfer accompanied by multiple complex parallel reversible chemical reactions. This model can be applied for the calculation of the mass transfer rates, enhancement factors and concentration profiles for a wide range of processes and conditions, for both film and penetration model. With the aid of this mass transfer model it is demonstrated that the absorption rates in systems with multiple reversible reactions can be substantially greater than the summation of the absorption rates derived for the single systems. This latter fact provides a scientific basis for the application of aqueous mixed amine solutions for industrial sour gas treating. Also it is shown that for kinetic studies by means of absorption experiments for reversible reactions the presence of small amounts of fast reacting contaminants can have an overruling effect on the outcome of the determination of the reaction kinetics. It is shown that the concepts of shuttle mechanism and homogeneous catalysis refer to asymptotic situations, for practical situations intermediate behaviour was observed which was previously not accessible for analysis. Experimentally determined absorption rates of CO₂ in aqueous solutions of various mixtures of alkanolamines (MMEA–MDEA, MEA–MDEA, DIPA–MDEA and MEA–DEA–MDEA) can be predicted extremely well for the several mass transfer regimes which were studied experimentally. The experiments were carried out in a stirred vessel with a flat surface over a wide range of process conditions.

1. INTRODUCTION

Absorption accompanied by chemical reactions has been studied intensively, but the major part of the studies has dealt with absorption followed by a single irreversible reaction. In case a reversible reaction occurs the description of this phenomenon is very complex due to the nonlinearity of the expressions for the reaction kinetics. Moreover, the equations of the mass transfer model (e.g. penetration or film theory) cannot be solved analytically and therefore numerical techniques must be used (Perry and Pigford, 1953; Secor and Beutler, 1967; Cornelisse *et al.*, 1980) to obtain an exact description of these processes. An alternative approach is approximate analytical solution of the equations as originally proposed by van Krevelen and Hoftijzer (1948), but the outcome of this procedure must be verified by means of a numerical solution because these approximations usually are not generally valid, see Part I.

In the process industry, operations accompanied by several parallel reversible chemical reactions occur very frequently. The theory of absorption followed by several parallel chemical reactions has been studied only for some special processes (Jhaveri, 1969; Alper, 1972, 1973; Li *et al.*, 1974; Chang and Rochelle, 1982). Onda *et al.* (1970) presented a few approximate solutions for specific cases.

A frequently encountered process in which two parallel reactions are occurring is the absorption of CO₂ (or H₂S) in an aqueous alkanolamine solution. In this solution the CO₂ (or H₂S) reacts with the alkanol-

amine and the hydroxyl ions which are present in the liquid due to the protonation of the amine. The latter reaction usually has only a very small effect because of the low concentration of hydroxyl ions for common values of K_a . However, in case of sterically hindered amines, which cannot form stable carbamates (Satori and Savage, 1983), this reaction may turn out to be dominant for the absorption rate. Another example is the removal of CO₂ by means of amine promoted carbonate processes (Savage *et al.*, 1984).

Moreover, it should be realized that even in the case of single gas absorption the amine gas-treating processes may still be processes where several parallel chemical reactions occur because the purity of the amine used is usually less than 100% (Versteeg and van Swaaij, 1988a), and frequently the contaminants are other very reactive amines. During the regeneration of the loaded solvent at high temperatures (Blauwhoff *et al.*, 1985; Kohl and Riesenfeld, 1979) also for pure amines degradation occurs and sometimes also fast reacting amines will be produced. A very recent development of amine gas-treating processes is the application of blends of amines (a solution of two or more amines in varying compositions) (Chakravarty *et al.*, 1985) in which the combination of the absorption characteristics of the amines is used on purpose, leading to an improvement of the treating process, especially if deep CO₂ removal is required.

In Part I the problem of mass transfer accompanied by a single complex reversible reaction was discussed.

An improved numerical technique was developed to solve the equations which describe this phenomenon for both the film and penetration theory.

In the present paper this technique was used to solve the equations which describe mass transfer accompanied by several parallel complex reversible chemical reactions.

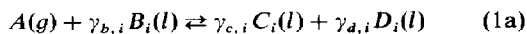
The calculations of the mass transfer rates according to this numerical solution method will be compared with the outcome of absorption experiments of CO₂ in several aqueous solutions of mixtures of alkanolamines with varying composition. The experiments have been carried out in a stirred vessel.

2. THEORY

2.1. Introduction

The problem considered is mass transfer of a single gas phase component accompanied by complex reversible parallel reactions of general order with respect to both reactants and products. For this study the parallel reactions were classified in three groups.

The first group consists of independent parallel reactions without a direct interaction between the products and/or reactants. These reactions can be presented schematically by:



for $i = 1, 2, 3, \dots, n$

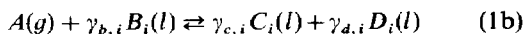
with the following reaction rate equations:

$$R_{a,i} = k_{m_i, n_i, p_i, q_i} [A]^{m_i} [B_i]^{n_i} [C_i]^{p_i} [D_i]^{q_i} - k_{r_i, s_i, t_i, v_i} [A]^{r_i} [B_i]^{s_i} [C_i]^{t_i} [D_i]^{v_i} \quad (2a)$$

for $i = 1, 2, 3, \dots, n$.

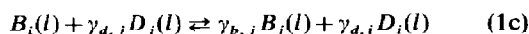
An example of this group of parallel reactions is the oxidation of both *p*-xylene and methyl-*p*-toluate for the production of dimethylterephthalate (Kirk-Othmer, 1978).

The second group consists of independent parallel reactions similar to the first group, but additional reactions take place between the products and the liquid phase reactants. For the second group the relevant reactions can be presented schematically by:



for $i = 1, 2, 3, \dots, n$

and direct interaction reaction:



for $j = 1, 2, \dots, n$ and $j \neq i$

for $i = 1, 2, 3, \dots, n$

with the following reaction rate equations:

$$R_{a,i} = k_{m_i, n_i, p_i, q_i} [A]^{m_i} [B_i]^{n_i} [C_i]^{p_i} [D_i]^{q_i} - k_{r_i, s_i, t_i, v_i} [A]^{r_i} [B_i]^{s_i} [C_i]^{t_i} [D_i]^{v_i} \quad (2b)$$

for $i = 1, 2, 3, \dots, n$

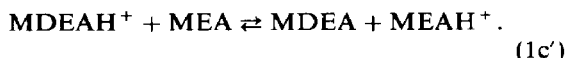
and

$$R_{b,i} = k_{m_i, n_i, p_i, q_i} [B_i]^{m_i} [D_j]^{n_j} [B_j]^{p_j} [D_i]^{q_i} - k_{r_i, s_j, t_j, v_i} [B_i]^{r_i} [D_j]^{s_j} [B_j]^{t_j} [D_i]^{v_i} \quad (2c)$$

for $j = 1, 2, \dots, n$ and $j \neq i$

for $i = 1, 2, 3, \dots, n$.

Examples of this group of parallel reactions with an interaction between the products and reactants is the absorption of CO₂ into a solution of a mixture of amines or the removal of CO₂ by means of amine-promoted carbonate processes. For the situation that CO₂ is absorbed in a mixture of mono-ethanol-amine (MEA) and di-methyl-ethanol-amine (MDEA) the interaction reactions (1c) reduce to one single reaction which is extremely fast as it involves only a proton transfer:



The third group of parallel reactions consists of reactions which have one common product *D* as is schematically presented by:



for $i = 1, 2, 3, \dots, n$

with the following reaction rate equations:

$$R_{a,i} = k_{m_i, n_i, p_i, q_i} [A]^{m_i} [B_i]^{n_i} [C_i]^{p_i} [D]^{q_i} - k_{r_i, s_i, t_i, v_i} [A]^{r_i} [B_i]^{s_i} [C_i]^{t_i} [D]^{v_i} \quad (2d)$$

for $i = 1, 2, 3, \dots, n$

An example of this group is the absorption of H₂S in a solution of a mixture of alkanolamines in which HS⁻ is the common reaction product for each reaction.

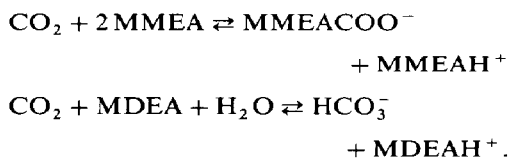
For the description of the three groups of mass transfer followed by parallel reversible chemical reactions both the penetration model and the film model have been applied for the liquid phase. The mass transfer in the gas phase was described with the stagnant film model. For the details of the numerical treatment the reader is referred to Part I.

2. EXPERIMENTAL

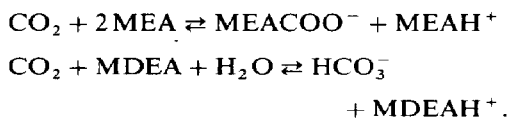
The models which were numerically solved in the present study have been experimentally tested by means of the absorption of CO₂ in aqueous solutions of mixtures of alkanolamines. The experiments were carried out in a stirred vessel operated under such conditions that the gas-liquid interface appeared visually to be completely smooth and therefore was well defined. The experimental set-up was identical to the one used by Versteeg and van Swaaij (1988a, b).

Five mixtures with varying composition have been studied at two temperatures. According to Blauwhoff *et al.* (1984) the following overall reactions between CO₂ and the various amines occur:

system 1: mixture of MDEA and methyl-mono-ethanol-amine (MMEA) at $T = 293$ K. The liquid composition consisted of 22 mol m^{-3} MMEA and 2010 mol m^{-3} MDEA. Commercial grade amines were used with 98% purity (Versteeg and van Swaaij, 1988a).

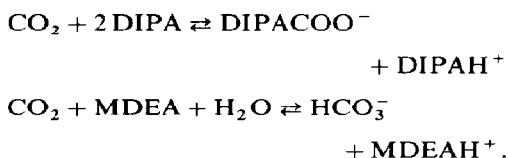


system 2: mixture of MDEA and MEA at $T = 293$ K. The liquid composition consisted of 37 mol m^{-3} MEA and 2990 mol m^{-3} MDEA.

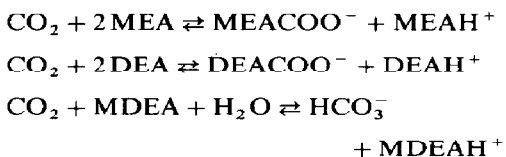


system 3: mixture of MDEA and MEA at $T = 293$ K. The liquid composition consisted of 37 mol m^{-3} MEA and 2114 mol m^{-3} MDEA. For this system the reactions are similar to mixture 2.

system 4: mixture of MDEA and di-iso-propanol-amine (DIPA) at $T = 298$ K. The liquid composition consisted of 826 mol m^{-3} DIPA and 1034 mol m^{-3} MDEA.



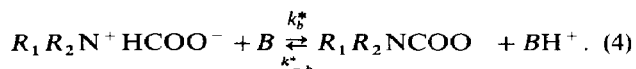
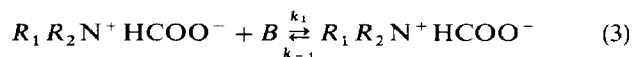
system 5: mixture of MDEA, MEA and di-ethanol-amine (DEA) at $T = 293$ K. The liquid composition consisted of 500 mol m^{-3} MEA, 1010 mol m^{-3} DEA and 2546 mol m^{-3} MDEA.



All the reactions of these systems are reversible reactions and interaction reactions like e.g. (1c') may occur between the amines and promoted amines. The various systems can be considered as parallel reactions without direct interaction, group 1, if reaction (1c) does not evolve at a substantial rate and extent, or with interaction, group 2. In this study both models (group 1 and group 2) were compared with the results of the experiments.

The reaction rate expressions of CO_2 and alkanolamines are usually very complex (Blauwhoff *et al.*,

1984) and therefore these expressions were approximated through relations like eq. (2a). However, before the kinetic constants for the rate expression according to eq. (2a) could be estimated, the reaction between CO_2 and primary and secondary alkanolamines was thoroughly studied because the mechanism which is now generally accepted for these reactions, the zwitterion mechanism (Danckwerts, 1979; Laddha and Danckwerts, 1981; Blauwhoff *et al.*, 1984; Barth *et al.*, 1984; Sada *et al.*, 1985; Versteeg and van Swaaij, 1988a, b), makes this calculation not so simple and straightforward. As was originally proposed by Blauwhoff *et al.* (1984) the reaction between CO_2 and these amines could be represented according to:



For this mechanism the overall forward reaction rate equation can be derived with the assumption of quasi-steady state condition for the zwitterion concentration:

$$R_{\text{CO}_2} = \frac{[\text{CO}_2][R_1 R_2 NH]}{\frac{1}{k_2} + \sum \frac{1}{k_b[B]}} \quad (5)$$

$$\text{met } k_b = \frac{k_{-1}}{k_2 k_b^*}.$$

All bases present in the liquid can contribute to the removal of the proton from the zwitterion in reaction (4) represented by $\Sigma 1/k_b[B]$. In aqueous solutions of one single amine the species water, OH^- -ions and the amine act as bases; whereas in mixtures of alkanolamines each amine can act as a base for this removal for all the occurring reactions.

For the calculation of the reaction rate constants necessary for the simulation of the experiments by means of the numerical model the contributions of the various amines to the proton removal of the zwitterion must be known, as for instance for mixture 4 the contribution of MDEA to the removal of the proton from the DIPA-zwitterion. In the open literature no data have been presented in which the reaction kinetics of mixtures of amines with CO_2 have been studied. Moreover, in all kinetic studies preferably amines of high purity were used. Therefore these contributions to the removal by amines different from the zwitterion were estimated with the aid of the relation between k_b and the $\text{p}K_{\text{abase}}$ as was proposed by Blauwhoff *et al.* (1984). The reverse reaction rate constants were estimated by considering that at equilibrium the forward and reverse reaction rates are equal, leading to:

$$K_i = \frac{k_{m_i, n_i, p_i, q_i}}{k_{r_i, s_i, t_i, v_i}} \quad (6)$$

The equilibrium composition of the loaded liquid was calculated according to the method proposed by Blauwhoff and van Swaaij (1980).

The resistance against mass transfer in the gas phase was neglected as only CO₂ of high purity was used as gas phase. The liquid-phase mass transfer coefficient was determined experimentally by means of the absorption of high purity N₂O into the solutions. For the simulation of the experiments the penetration model has been applied, as for stirred vessels this model was expected to be the most realistic one (Versteeg *et al.*, 1987).

The physico-chemical constants, solubility and diffusivity, of CO₂ in the solutions were obtained by means of the CO₂-N₂O analogy (Laddha *et al.*, 1981). The diffusivities of the reactive solutes and the products were estimated by means of a modified Stokes-Einstein relation (Versteeg and van Swaaij, 1988c). For the ionic products, the diffusivity has been given the same value for each species in order to assure overall electroneutrality in the liquid phase and the values were taken equal to the component with the lowest diffusivity.

3. RESULTS

It is obvious that it is impossible, due to the large number of parameters, which can be varied over a wide range, to present an extensive number of simulations. Therefore only a few typical situations and processes have been studied for each group of parallel reactions.

3.1. Parallel reactions without interaction

For this group of parallel reactions only numerical simulations and no experiments have been carried out.

For irreversible reactions it can easily be shown that the enhancement factor for the process with parallel reactions is smaller than or equal to the summation of the individual enhancement factors of the single reactions. In case all reactions can be regarded as instantaneous with respect to mass transfer an expression can be derived (Westerterp *et al.*, 1984) for the enhancement factor for this system, according to the film model:

$$E_{\text{inf.,multiple}} = \sum_{j=1}^n (E_{\text{inf.,single}} - 1) + 1 \quad (7)$$

and the maximum attainable individual enhancement factor can be calculated with:

$$E_{\text{inf.,single}} = 1 + \frac{D_b[B_j]}{v_{bj}D_a[A]_{\text{int}}} \quad (8)$$

For the asymptotic situation of pseudo first-order reaction kinetics (Hatta-number > 2) for the single reactions, the enhancement factor for the multiple reaction process can be derived (Westerterp *et al.*, 1984):

$$E_{\text{multiple}} = \sqrt{\sum_{j=1}^n (E_{\text{single},j})^2} \quad (9)$$

with:

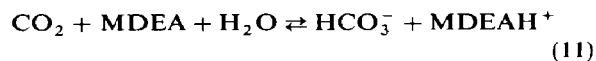
$$E_j = Ha_j = \frac{\sqrt{k_n[B_j]^n D_a}}{k_t} \quad (10)$$

The third asymptotic situation occurs in case of slow reaction rates, no enhancement of the absorption process occurs, and the enhancement factor is equal to unity for both the single and multiple reactions.

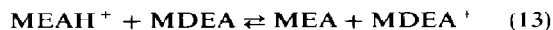
In case the reactions are reversible it is not possible to predict the overall enhancement factor of the absorption process by means of equations similar to (7) and (9). The effect of reversibility was simulated with the numerically solved model. However, due to the large number of parameters which can affect the absorption rate and so the enhancement factor, the outcome of the calculations for only two processes will be presented in this work. The first process studied was the absorption of CO₂ in aqueous solutions of MDEA and MEA. The other situation looked upon was the absorption of a solute into a liquid in which two similar parallel reactions occurred.

The absorption of CO₂ in aqueous alkanolamine solutions is studied frequently because of its importance for gas-treating processes. However, often the amines used for these studies are contaminated with small amounts of other, usually fast-reacting, amines. Therefore in this work the effect of small amounts of MEA in aqueous MDEA solutions was calculated with the aid of the mass transfer model. Thus simulating CO₂ absorption into MDEA solutions containing one or more reactive impurities or degradation products.

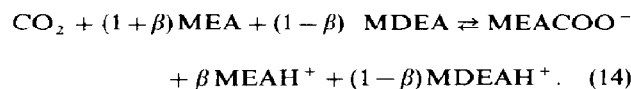
The following two reactions take place:



In fact the second reaction expression is not entirely correct because a part of the protonated MEA will transfer its proton to MDEA, which is present in the liquid in excess according to:



and therefore the overall reaction expression between CO₂ and MEA in the presence of MDEA is presented correctly by:



The value of β depends on the protonation constants (K_a) of the amines involved and the liquid composition.

In the simulations this effect was not taken into account because it will be extensively treated in the model of parallel reactions with interaction. Moreover, the calculations were carried out in order to study the effect of small amounts of contaminants on the absorption rate for parallel reactions without interaction. In Table 1 the data are presented which

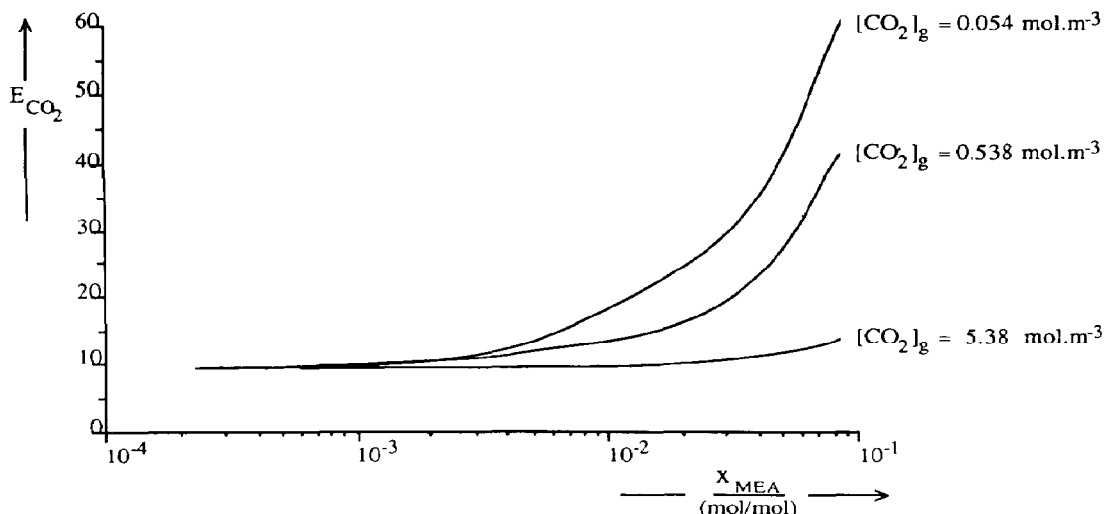


Fig. 1. Effects of the MEA-fraction on the calculated enhancement factor for an aqueous MEA-MDEA mixture and $\alpha_{\text{CO}_2} = 0.05$.

Table 1. Conditions for the simulation for the system MEA-MDEA without interaction

$[\text{Amine}]_{\text{tot.}}$	2000 mol m^{-3}
k_i	$1 \times 10^{-5} \text{ m s}^{-1}$
k_a	$1 \times 10^2 \text{ m s}^{-1}$
$k_{1,1}(\text{MDEA})$	$4.69 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$k_{-1,-1}(\text{MDEA})$	$3.18 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$k_{1,1}(\text{MEA})$	$5.87 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$k_{-1,-1}(\text{MEA})$	$1.54 \times 10^{-4} \text{ s}^{-1}$

were used for the simulations. For the determination of the physical constants the reader is referred to Versteeg and van Swaaij (1988c).

In Fig. 1 the enhancement factor calculated according to the model is presented as function of the molar fraction of MEA for three CO_2 gas-phase concentrations and a CO_2 liquid-loading, α_{CO_2} , of 0.05. Similar calculations were performed for a liquid loading, $\alpha_{\text{CO}_2} = 0.01$. From both simulations it can be concluded that small amounts of MEA have a pronounced effect on the enhancement factor even for CO_2 -loadings that could imply that no MEA is present in the liquid anymore if CO_2 would react irreversibly and preferentially with MEA. The influence of the small amount of MEA is more substantial for low CO_2 gas-phase concentrations. This can be explained easily if the individual enhancement factors are calculated for the single reactions. For MDEA the absorption process takes place in the pseudo first-order regime for all conditions, and for MEA the absorption regime depends on the gas-phase concentration and changes gradually from the instantaneous regime (high P_{CO_2}) to the pseudo first-order regime (low P_{CO_2}). Due to the low MEA-concentrations the enhancement factor in the instantaneous regime, $E_{\text{inf.}}$, is nearly equal to unity for high CO_2 gas-phase concentrations and therefore hardly any influence of the presence of MEA on the

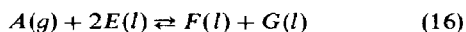
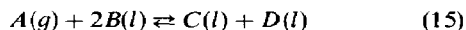
enhancement factor for the parallel process is observed. In case of low CO_2 gas-phase concentrations the enhancement factor for the MEA reaction ultimately becomes equal to the Ha -number which is characteristic for the pseudo first-order regime. For the latter situation the overall enhancement factor for the parallel process can be estimated with eq. (9) because both reactions of CO_2 with the amines may be regarded as irreversible for the conditions studied.

This system consists of a mixture of a fast reacting component of a low concentration in combination with a slow reacting component of a high concentration, and the influence of MEA on the enhancement factor (absorption rate) is considerable even for high CO_2 -loadings (see Fig. 1) this effect can be explained according to the so-called shuttle-mechanism. The shuttle-mechanism (Astarita *et al.*, 1981) describes the process as two parallel reactions, and the fast reacting component is regenerated by means of the interaction of the equilibrium reactions in the liquid bulk. For the shuttle-mechanism the enhancement factor can be calculated analytically only for pseudo-irreversible reactions and the two asymptotic situations of instantaneous reaction regime [eq. (7)] and the pseudo first-order reaction regime [eq. (9)] respectively. In the intermediate regimes and for reversible reactions numerical solution of the equations which describe this phenomenon is required. From the fact that for one asymptotic situation of the simulations the enhancement factor for the multiple process can be calculated according to eq. (9), which was derived for irreversible reactions, it can be concluded that MEA is basically regenerated in the liquid bulk and therefore the shuttle-mechanism applies to this situation.

From the simulations it can be concluded that for kinetic studies by means of absorption experiments the presence of small amounts of fast reacting contaminants can have an overruling effect on the absorp-

tion rate depending on the experimental conditions. Therefore it is necessary to check the influence of contaminants with a mass transfer model in order to be able to choose suitable experimental conditions and to determine the reaction kinetics correctly.

The second system that was simulated consisted of two parallel reactions with a moderate and a low value of the equilibrium constant respectively. Both reactions had identical reaction equations:



and identical reaction rate equations:

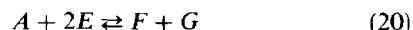
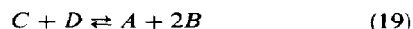
$$R_{A,1} = k_{1,2}[A][B]^2 - k_{-1,-1}[C][D] \quad (17)$$

$$R_{A,2} = k_{2,2}[A][E]^2 - k_{-2,-1}[F][G]. \quad (18)$$

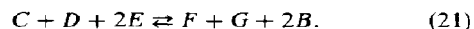
Examples of this system are mixtures of primary and/or secondary amines, e.g. MEA-MMEA or AMP (amino-methyl-propanol)-DEA. In this system also one of the reactants (*B*) can be regarded as a contamination which is present in the liquid in a very low concentration. In Table 2 the values of the physico-chemical constants which were used for the calculations of the enhancement factors and concentration profiles are presented.

In Table 3 the outcome of the calculations for the enhancement factor is presented together with the enhancement factor which would be attained if the simulations were performed for the individual systems. The first reaction (eq. 15) is instantaneous with respect to mass transfer and the second reaction (eq. 16) can be regarded as a pseudo first-order reaction as can be calculated from the data presented in Table 2. Contrary to the situation for irreversible reactions the

enhancement factor for reversible multiple reactions can be substantially higher, as can be seen in Table 3. This striking effect can be explained if the concentration profile in the elements as conceived in the penetration theory at the end of the contact time of the multiple system is compared with those of the single systems, see Fig. 2, case 1. It should be noted that both concentration and spatial coordinates are dimensionless. The slopes of the profiles of the non-volatile components are equal to zero at the interface, however, this cannot be concluded always directly from the figures. The liquid-phase components are normalized on the bulk concentrations of each reactant respectively, and the gas-phase component on the bulk gas-phase concentration corrected for the solubility. From Fig. 2 it can be concluded that due to the presence of *E* the concentration of *B* near the gas-liquid interface was increased by the reactions (15) and (16) according to:



and although no direct interaction exists, an equilibrium shift reaction has the following effect:



Near the reaction zone component *B* is regenerated by component *E* from the reaction products *C* and *D* with the simultaneous production of the other reaction products *F* and *G*. This regeneration of *B* reduces its diffusion limitation from the liquid bulk to the interface and therefore an essentially higher concentration of *B* is present near the interface and therefore the overall enhancement factor will be increased.

In Fig. 3 the concentration profiles for case 2 are presented for the system with the parallel reactions. In this figure it can be seen that the concentration of *B* is locally even greater than the liquid bulk concentration. This implies that the production of *B* according to (21) exceeds the transport to the bulk by means of molecular diffusion.

For this process the shuttle-mechanism is not able to explain the observed results as the fast reacting component is completely regenerated near the gas-liquid interface. According to Astarita *et al.* (1981) this situation seems to be similar to the homogeneous catalysis mechanism which assumes an instantaneous regeneration of the fast reacting component. However, this mechanism is basically identical to an increase of the reaction rate constant and in fact the system with parallel reactions reduces to a system with only one reaction. It should be noted that the mechanisms proposed to describe the observed phenomena, shuttle-mechanism and homogeneous catalysis, are only valid for asymptotic situations and processes with irreversible reactions. For reversible processes approximate solutions of these mechanisms are not generally valid and their applicability is therefore very restricted. With the model presented in this work no restrictions are imposed and it is valid for all asymptotic situations and the intermediate regions.

Table 2. Conditions for the simulation for the system $A + 2B$ and $A + 2E$ without interaction

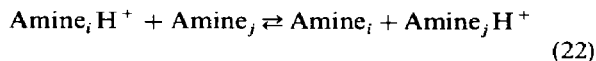
$[A]_g$	0.1 mol m ⁻³
$[B]$	100 mol m ⁻³
$[E]$	2000 mol m ⁻³
He	0.60 mol mol ⁻¹
k_i	1×10^{-3} m s ⁻¹
k_g	1×10^2 m s ⁻¹
$k_{1,2}(B)$	1×10^6 m ⁶ mol ⁻² s ⁻¹
$k_{-1,-1}(B)$	1×10^5 m ³ mol ⁻¹ s ⁻¹
$k_{1,2}(A)$	1×10^{-3} m ⁶ mol ⁻² s ⁻¹
$k_{-1,-1}(A)$	1×10^{-5} m ³ mol ⁻¹ s ⁻¹
Case 1	$D_i = 1 \times 10^{-9}$ m ² s ⁻¹
Case 2	$D_g = 1 \times 10^{-10}$ m ² s ⁻¹
Case 3	$D_E = 1 \times 10^{-10}$ m ² s ⁻¹
Case 4	$D_C = D_D = 1 \times 10^{-10}$ m ² s ⁻¹

Table 3. Results simulation for the system $A + 2B$ and $A + 2E$ without interaction

	Case 1	Case 2	Case 3	Case 4
$E_{[eq. (32)]}$	507	221	507	276
$E_{[eq. (33)]}$	198	198	194	198
$E_{parallel}$	2530	792	2257	1499

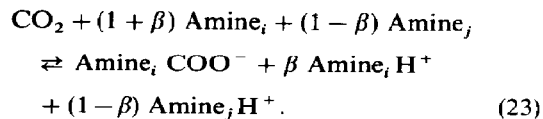
3.2. Parallel reactions with interaction

For this group of multiple parallel reactions absorption experiments of CO_2 in aqueous solutions of mixtures of amines have been carried out and are compared with the outcome of the numerical simulations. In these aqueous solutions, simultaneous with the reaction between CO_2 and the amines, additional reactions occur between the protonated amines and the unprotonated amines according to:



and for the situation that one of the amines is a primary or secondary amine this eventually leads to

the following overall reaction equation for the reaction with CO_2 :



Due to the implementation of eq. (22) in the mass transfer model this change in the stoichiometry of the reaction between CO_2 and the several amines has been taken into account.

Mixture of MMEA and MDEA. In Table 4 the experimental conditions are summarized. This com-

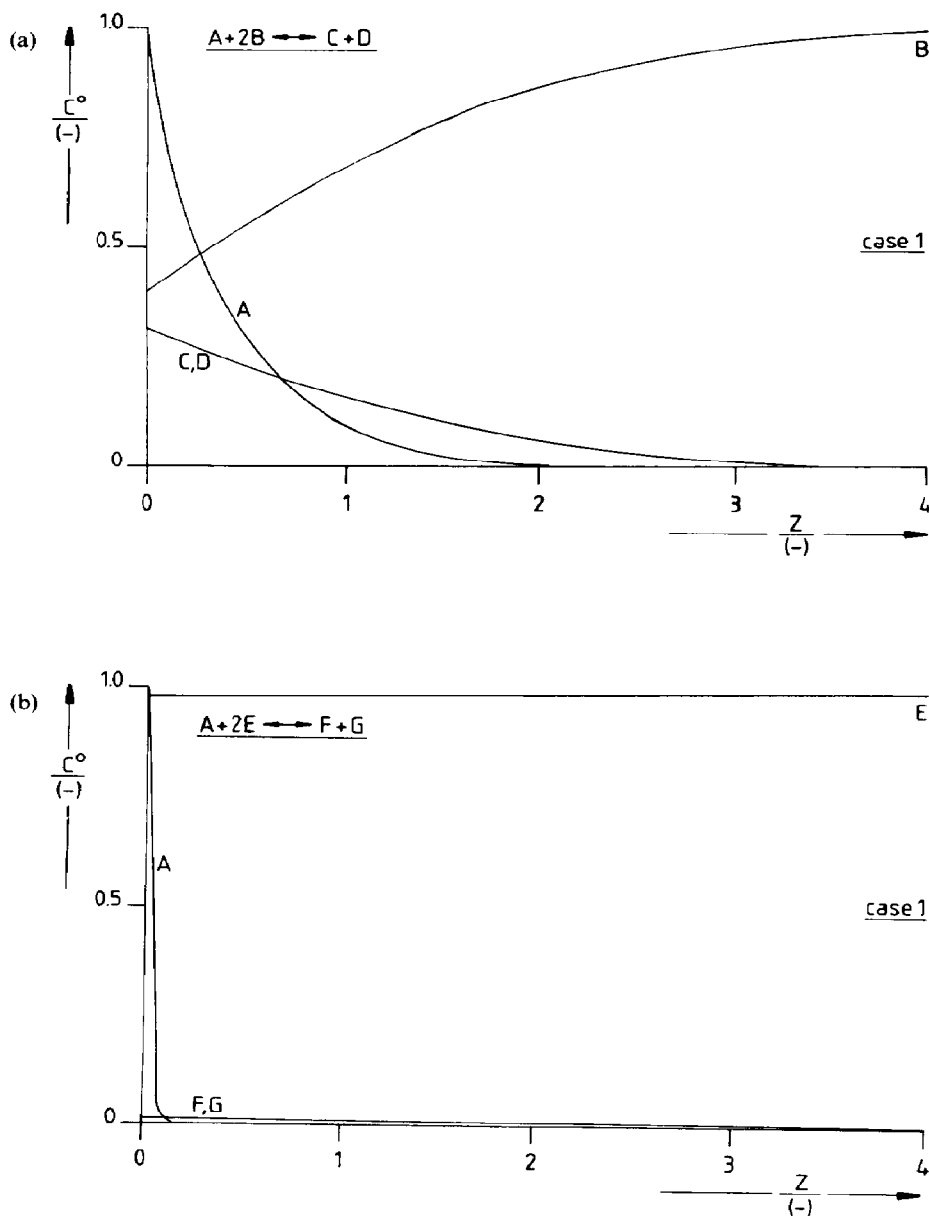


Fig. 2. (a) and (b).

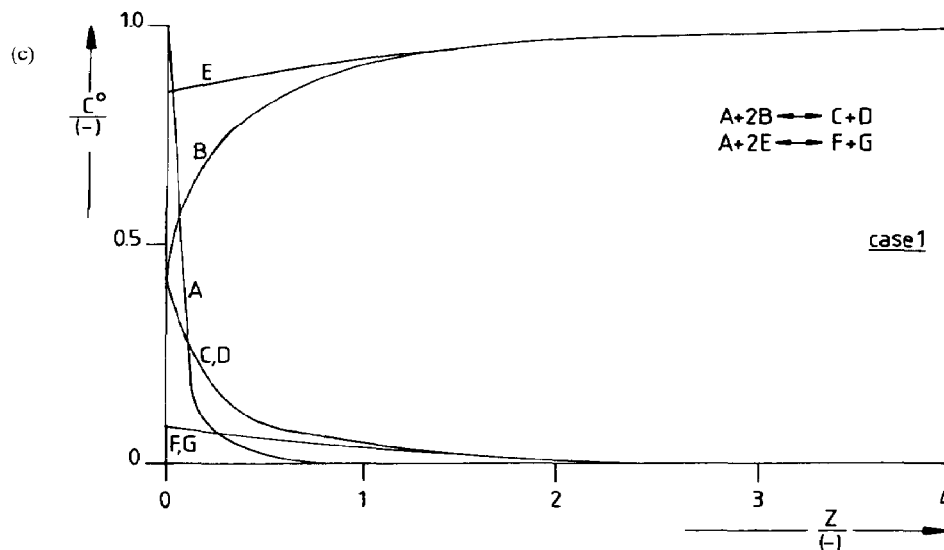


Fig. 2. Dimensionless concentration profiles for (a) the system $A + 2B \leftrightarrow C + D$, (b) the system $A + 2E \leftrightarrow F + G$, (c) the system $A + 2B \leftrightarrow C + D$ and $A + 2E \leftrightarrow F + G$.

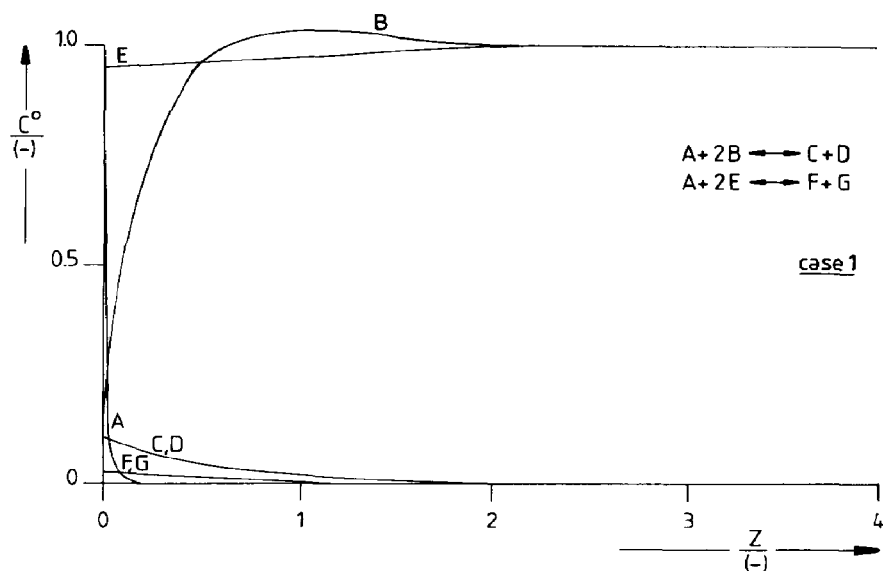


Fig. 3. Dimensionless concentration profiles for the system $A + 2B \leftrightarrow C + D$ and $A + 2E \leftrightarrow F + G$.

position can be regarded as an MDEA solution contaminated with a small amount of MMEA. In Fig. 4 the experimental results are compared with the outcome of the numerical simulations and from this figure it can be concluded that the model presented in this work is able to calculate the molar flux for this system extremely well.

In Fig. 5 a typical example of the liquid concentration profiles at the end of the contact time is presented for a high CO_2 gas-phase concentration. In this figure can be seen that the MMEA concentration decreases substantially towards the interface and

therefore the reaction between CO_2 and MMEA can be regarded as instantaneous with respect to mass transfer. Nearly all of the protons of MMEA^+ are transferred to MDEA which can be concluded from the profiles of MDEACOO^- and MMEA^+ leading to $\beta = 0$ in eq. (23) because in the absence of reaction (22) both profiles must be similar. Moreover, the difference between these concentrations must remain constant and equal to that in the liquid bulk in case that $\beta = 1$; however, this only occurs in case of equal diffusivities for both components.

It should be noted that the slopes near the interface

Table 4. Conditions for the experiments for the system CO_2 -MMEA-MDEA

$0.103 \leq [\text{CO}_2]_g \leq 0.823 \text{ mol m}^{-3}$
$1.59 \leq [\text{CO}_2]_l \leq 19.7 \text{ mol m}^{-3}$
$k_l = 6.25 \times 10^{-6} \text{ m s}^{-1}$
$[\text{MMEA}] = 22 \text{ mol m}^{-3}$
$[\text{MDEA}] = 2010 \text{ mol m}^{-3}$
$He_{\text{CO}_2} = 0.806$
$T = 293 \text{ K}$

of all components except that for CO_2 are equal to zero, this may not be directly clear from the presented concentration profiles.

In Fig. 6 the experimental results are compared with the outcome of the calculations of the model without interaction, i.e. $\beta = 1$. From Fig. 6 can be concluded that a substantial discrepancy exists between the experimental and numerical results. This can be explained easily from the fact that for nearly all conditions studied the reaction between CO_2 and MMEA

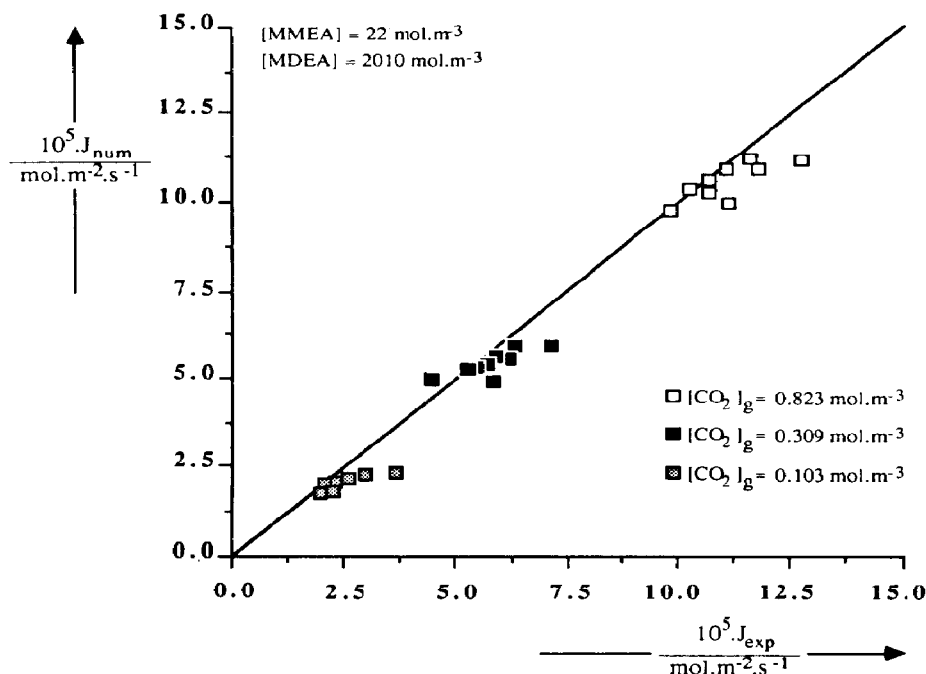


Fig. 4. Comparison between the measured and the calculated absorption rates of CO_2 in an aqueous mixture of MMEA and MDEA for the model with interaction.

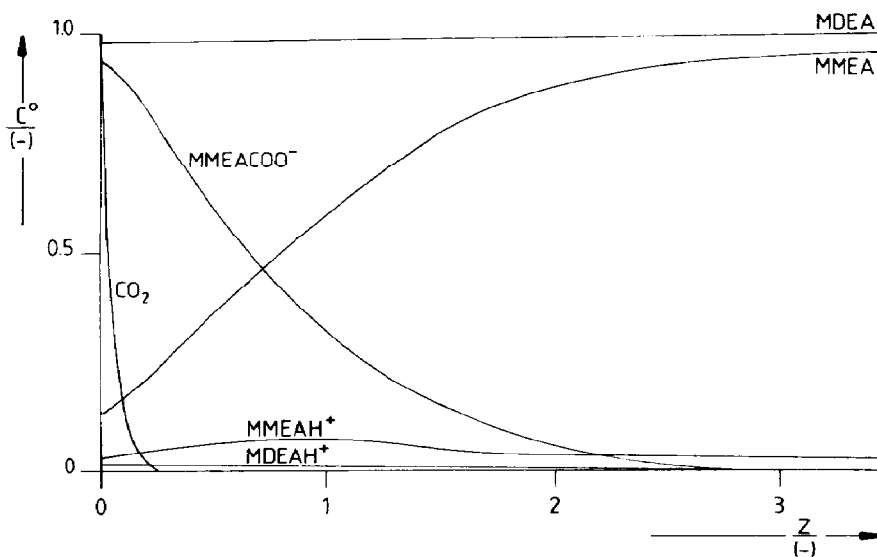


Fig. 5. Dimensionless concentration profiles for the system CO_2 -MMEA-MDEA at a high P_{CO_2} .

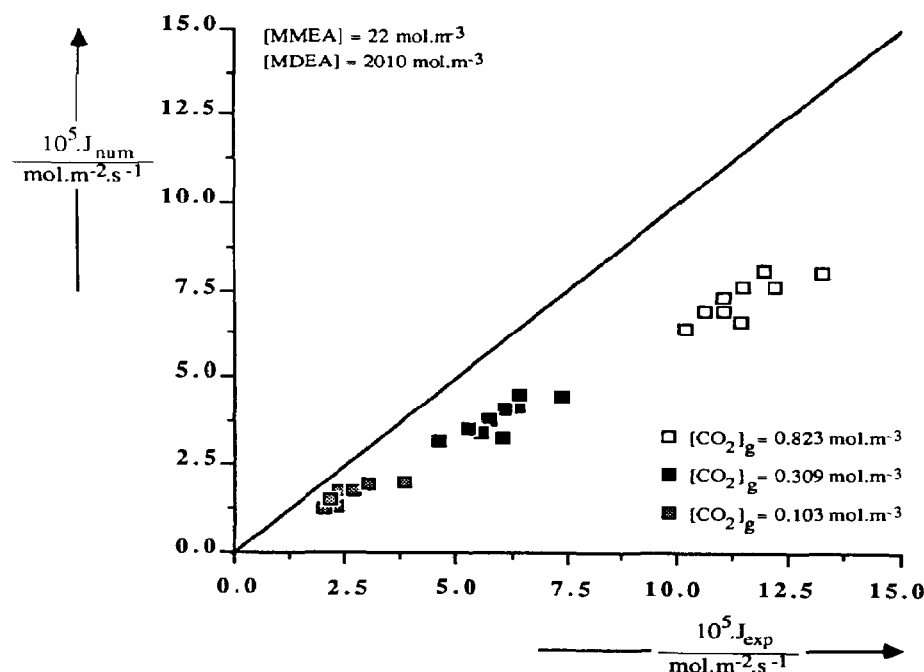


Fig. 6. Comparison between the measured and the calculated absorption rates of CO_2 in an aqueous mixture of MMEA and MDEA for the model without interaction.

can be regarded as instantaneous with respect to mass transfer. Therefore the enhancement factor is equal to E_{inf} to eq (8), in case no interaction occurs, the stoichiometric coefficient of MMEA, $\nu_{b,\text{MMEA}}$, is equal to 2 thus leading to a lower enhancement factor compared to situation with interaction where $\nu_{b,\text{MMEA}} \approx 1$.

The experimentally observed absorption rates can be predicted with the absorption model within an accuracy of about 20%.

Mixture of MEA and MDEA. In Table 5 the experimental conditions are summarized. In Fig. 7 the experimental results for the system 2 are compared with the outcome of the numerical simulations of the model. Similar to the system MMEA–MDEA it could be concluded from the calculated concentration profiles that the reaction between MEA and CO_2 is instantaneous with respect to mass transfer. Therefore reaction (22) has a large effect on the absorption rates. From the data in Table 5 it is possible to approximate the absorption region with eqs (8) and (10).

The results of the comparison for the system 3 are presented in Fig. 8. For the major part of the experimental conditions the reactions between CO_2 and both MEA and MDEA turned out to be pseudo first-order reactions and for this regime reaction (22) has no noticeable effect on the absorption rate.

From these figures it can be concluded that also for this mixture of amines the present model is able to predict the absorption rates within 20%.

Mixture of DIPA and MDEA. In Table 6 the

Table 5. Conditions for the experiments for the system CO_2 –MEA–MDEA

$0.274 \leq [\text{CO}_2]_g \leq 1.10 \text{ mol m}^{-3}$
$3.94 \leq [\text{CO}_2]_l \leq 214 \text{ mol m}^{-3}$
$k_l = 7.20 \times 10^{-6} \text{ m s}^{-1}$
$[\text{MEA}] = 85 \text{ mol m}^{-3}$
$[\text{MDEA}] = 2114 \text{ mol m}^{-3}$
$He_{\text{CO}_2} = 0.798$
$T = 293 \text{ K}$

$0.274 \leq [\text{CO}_2]_g \leq 8.20 \text{ mol m}^{-3}$
$4.00 \leq [\text{CO}_2]_l \leq 242 \text{ mol m}^{-3}$
$k_l = 5.45 \times 10^{-6} \text{ m s}^{-1}$
$[\text{MMEA}] = 37 \text{ mol m}^{-3}$
$[\text{MDEA}] = 2990 \text{ mol m}^{-3}$
$He_{\text{CO}_2} = 0.679$
$T = 293 \text{ K}$

Table 6. Conditions for the experiments for the system CO_2 –DIPA–MDEA

$0.274 \leq [\text{CO}_2]_g \leq 2.69 \text{ mol m}^{-3}$
$6.00 \leq [\text{CO}_2]_l \leq 223 \text{ mol m}^{-3}$
$k_l = 1.01 \times 10^{-5} \text{ m s}^{-1}$
$[\text{DIPA}] = 826 \text{ mol m}^{-3}$
$[\text{MDEA}] = 1034 \text{ mol m}^{-3}$
$He_{\text{CO}_2} = 0.722$
$T = 298 \text{ K}$

experimental conditions are summarized. The experimental results are compared with the outcome of the numerical simulations in Fig. 9. From this figure it can be concluded that the model is able to predict the

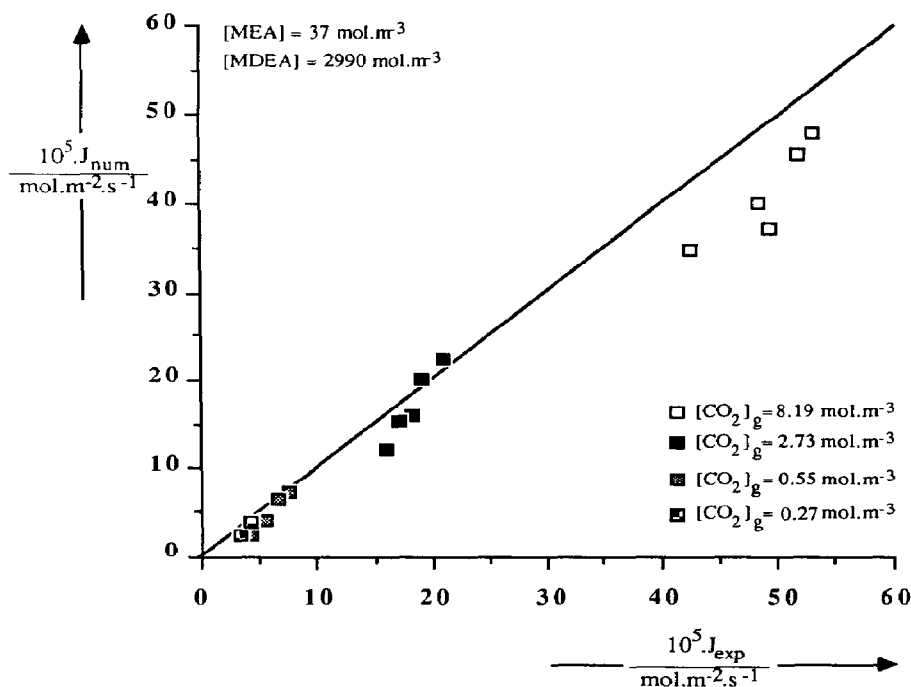


Fig. 7. Comparison between the measured and the calculated absorption rates of CO_2 in an aqueous mixture of MEA and MDEA.

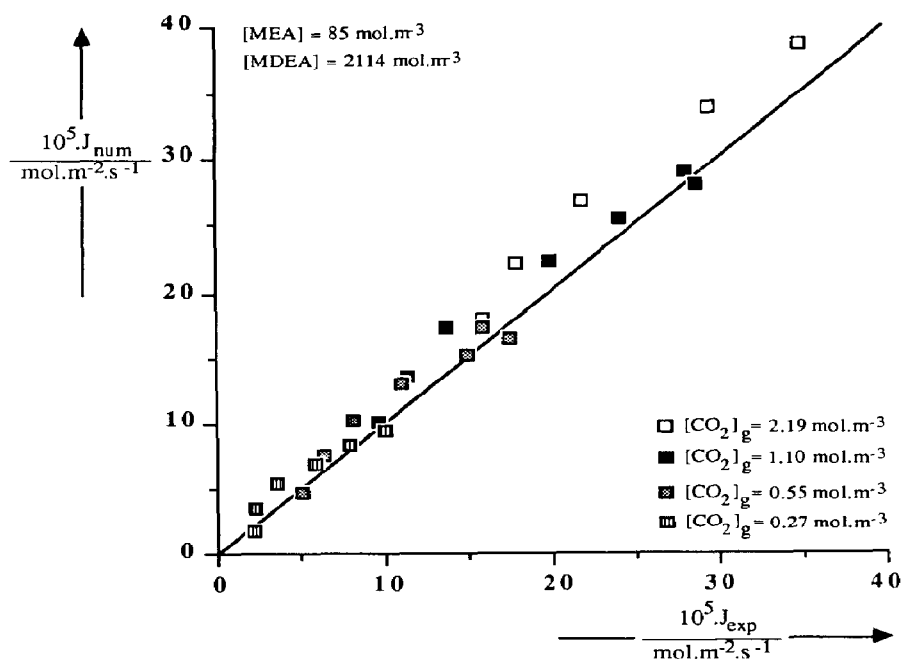


Fig. 8. Comparison between the measured and the calculated absorption rates of CO_2 in an aqueous mixture of MEA and MDEA.

absorption rates fairly well with deviations up to 40%. For all experiments the conditions for pseudo first-order reaction kinetics were practically always fulfilled and therefore the outcome of the calculations is deter-

mined mainly by the reaction rate constant for the reaction between CO_2 and DIPA. It should be noted that the reaction rate constant for the deprotonation of the zwitterion by MDEA was calculated from the

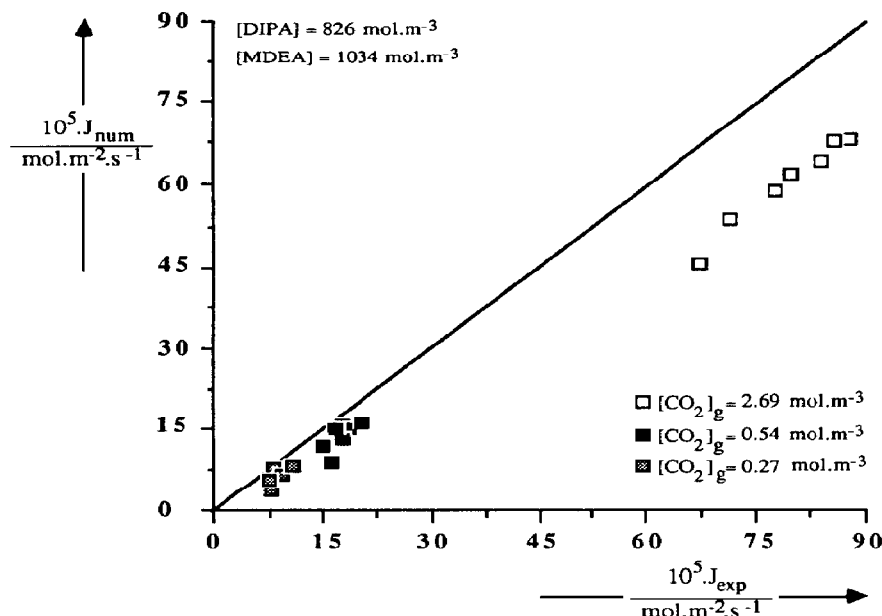


Fig. 9. Comparison between the measured and the calculated absorption rates of CO_2 in an aqueous mixture of DIPA and MDEA.

Table 7. Conditions for the experiments for the system CO_2 -MEA-DEA-MDEA

$0.274 \leq [\text{CO}_2]_g \leq 16.2 \text{ mol m}^{-3}$
$15.7 \leq [\text{CO}_2]_l \leq 670 \text{ mol m}^{-3}$
$3.60 \times 10^{-6} \text{ m s}^{-1} \leq k_l \leq 5.60 \times 10^{-6} \text{ m s}^{-1}$
$[\text{MEA}] = 500 \text{ mol m}^{-3}$
$[\text{DEA}] = 1010 \text{ mol m}^{-3}$
$[\text{MDEA}] = 2546 \text{ mol m}^{-3}$
$H_{\text{CO}_2} = 0.662$
$T = 293 \text{ K}$

results of Blauwhoff *et al.* (1984), who suggested a relation between the deprotonation rate constant and the $\text{p}K_{\text{a,base}}$. Therefore this value must be regarded as a rough estimation only.

Mixture of MEA, DEA and MDEA. In Table 7 the experimental conditions are summarized. The experimental results are compared with the outcome of the numerical simulations in Fig. 10. From this figure it can be concluded that the model is able to predict the absorption rates satisfactory within 35%. The average deviation between the experimental results and the numerical calculations for this mixture is greater compared to those observed for the other systems, this probably can be ascertained to the large number of parameters which have to be estimated as for instance the diffusivities of the ionic species. Especially for the instantaneous reaction regime the values of the diffusivity have a pronounced effect on the outcome of the calculations.

In Fig. 11 a typical example of the concentration profiles is presented. From these concentration profiles it can be concluded that the reaction of CO_2 and the

amines can be regarded as an instantaneous reaction and in this figure it can be seen that nearly all the protons produced by the various reactions are transferred to MDEA and that $\beta \rightarrow 0$ for both the reactions [eq. (14)] between CO_2 and MEA and DEA respectively. For absorption in the pseudo first-order regime the calculated enhancement factor is equal to the summation of the enhancement of the individual reactions between CO_2 and the amine.

3.3. Parallel reactions with a common product

For this group of parallel reactions only numerical simulations have been carried out. Actually, this group of parallel reactions can be considered as a mixture of the previous two groups, i.e. independent parallel reactions with an interaction by means of the common product. Therefore it can be expected that the phenomena observed for the other groups will occur also for this group.

4. DISCUSSION

The direct implementation of complex absorption models in for instance column calculations is until now very restricted due to the required amount of computational time. However, these kind of models can be very helpful to study absorption regimes which may occur during an absorption process. From the obtained numerical results and concentration profiles an approximation of the actual process can be derived which can be applied in the computational procedures for the column calculations.

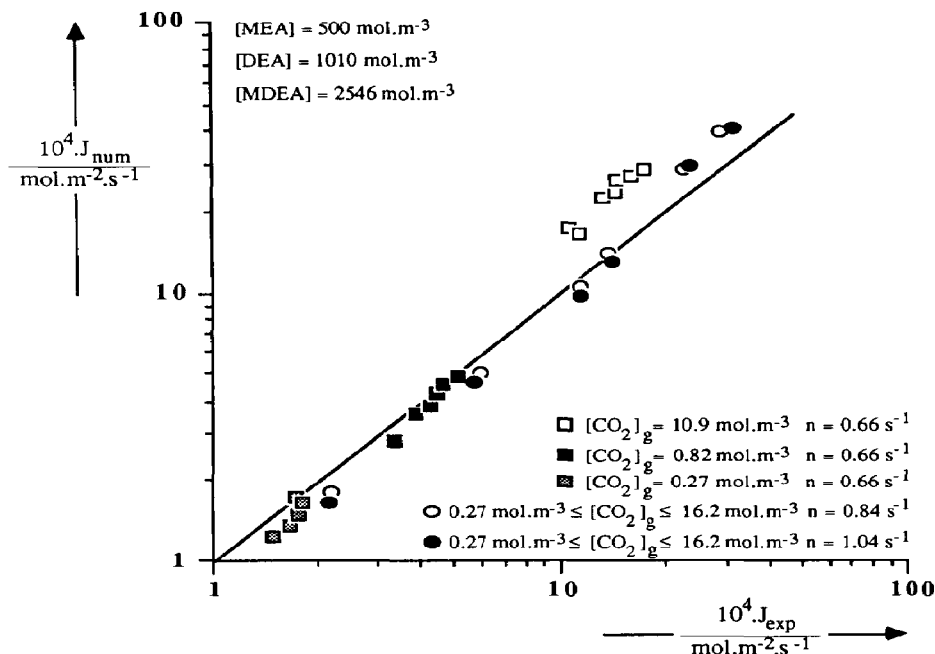


Fig. 10. Comparison between the measured and the calculated absorption rates of CO_2 in an aqueous mixture of MEA, DEA and MDEA.

The above-mentioned procedure, the derivation of an approximated, simple description of the absorption process with the aid of numerically solved model in which all possible interactions have been taken into account, has not been proposed in literature so far. Actually, the reverse action, afterwards numerical verification of approximated solutions, has been presented (Onda *et al.*, 1970), although often this verification has been excluded for a variety of reasons (Astarita *et al.*, 1981; DeCoursey, 1982).

It is clear that due to large number of parameters it is impossible to incorporate the numerical results into a simple, general applicable correlation of one sort or another.

Another possible way to incorporate the present model into an overall absorption module is variation of the number of grid points. In Part I it is shown that due to the additional transformations even for a small number of grid points (e.g. 10×10), which requires only a negligible amount of computational time, a satisfactory accuracy can be obtained already. If constant concentration profiles over the absorber are reached after several column interactions, the number of grid points can be increased to increase the overall accuracy.

5. CONCLUSIONS

The absorption rates for mass transfer accompanied by various groups of parallel reversible chemical reac-

tions can be calculated over a wide range of liquid compositions, number of reactions and process conditions with the numerical solution method presented in this study.

From the outcome of the calculations for systems consisting of several different reversible reactions it can be concluded that the enhancement factor for the multiple reactions system can be substantially higher than the summation of the enhancement factors for the single reactions. This effect was not observed for irreversible reactions where the enhancement for the multiple system is always smaller than the summation of the single reactions.

It is shown that for kinetic studies by means of absorption experiments for reversible reactions the presence of small amounts of fast reacting contaminants can have an overruling effect on the outcome of the determination of the reaction kinetics.

The numerical mass transfer model is able to predict extremely well the experimentally observed absorption rates of CO_2 in aqueous solutions of mixtures of various amines. As already mentioned in Part I, the discrepancy between the simulations and the experiments may be attributed to the occurrence of interfacial turbulence (Marangoni effects).

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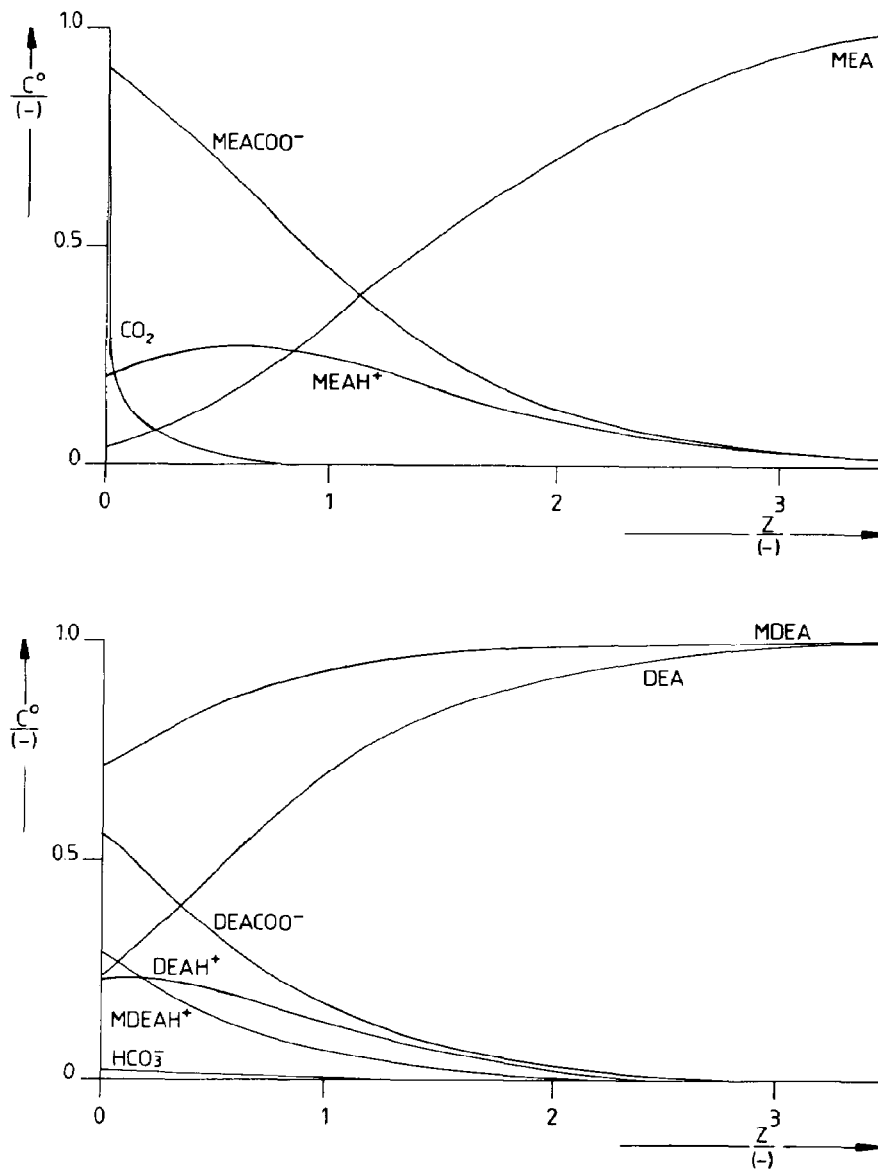


Fig. 11. Dimensionless concentration profiles for the system CO_2 -MEA-DEA-MDEA at a high P_{CO_2} .

NOTATION			
A	component A	He	dimensionless solubility defined as $[A]_l/[A]_g$, 1
B	component B	J	flux, molar $\text{m}^{-2} \text{s}^{-1}$
C	component C	K	equilibrium constant, $\text{mol}^{(-\gamma_a - \gamma_g + \gamma_c + \gamma_d)} \text{m}^{-3(-\gamma_a - \gamma_b + \gamma_c + \gamma_d)}$
D	component D	k_g	gas-phase mass transfer coefficient, m s^{-1}
$D_{\text{subscript}}$	diffusivity, $\text{m}^2 \text{s}^{-1}$	k_l	liquid-phase mass transfer coefficient, m s^{-1}
E	component E	$k_{\text{subscript}}$	reaction rate constant, $\text{m}^{3(m+n+p+q-l)} \text{mol}^{-(m+n+p+q-1)} \text{s}^{-1}$ or $\text{m}^{3(r+s+t+v-l)} \text{mol}^{-(r+s+t+v-1)} \text{s}^{-1}$
$E_{\text{subscript}}$	enhancement factor defined by eq. (14) or (15), 1	l	liquid phase
$E_{\text{subscript}, \infty}$	infinite enhancement factor defined by eq. (25), 1	m	reaction order, 1
F	component F	n	reaction order, 1
G	component G	p	reaction, order, 1
g	gas phase	q	reaction order, 1
Ha	Hatta-number defined by $(k_{m,n,p,q}[A]^{m-1}[B]^n[C]^p[D]^q D_a)^{0.5}/k_l$, 1		

R	reaction rate, $\text{mol m}^{-3} \text{s}^{-1}$
r	reaction order, 1
s	reaction order, 1
t	time variable, s
t	reaction order, 1
v	reaction order, 1
$[]$	liquid-phase concentration, mol m^{-3}

Greek letters

β	constant defined by eq. (14)
α	solute loading defined by $[A]_t/[B]_t$, 1
δ	film thickness according to the film model, m
θ	contact time according to the penetration model, s

Subscripts

a	component A
an	analytical solution
b	component B
$bulk$	concentration at bulk conditions
c	component C
d	component D
e	equilibrium
f	component F
g	component G
g	gas phase
i	interface or species i
$inf.$	maximum attainable
$ir.$	irreversible
m	maximum value
num	numerical solution
o	equilibrium composition
rev	reversible
t	total

Superscript

o	dimensionless
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